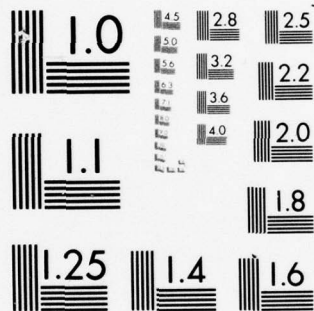


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gem-CHLORO (TRIMETHYLSILYL) ALLYL LITHIUM:  
A NOVEL AMBIDENT NUCLEOPHILE

by

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gem-Chloro(trimethylsilyl)allyllithium: A Novel Ambident Nucleophile

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SUMMARY

gem-Chloro(trimethylsilyl)allyllithium,  $\text{Li}[\text{Me}_3\text{SiCClCHCH}_2]$ , was prepared by the transmetalation reaction between  $\text{Ph}_3\text{PbCH}_2\text{-CH=C(Cl)SiMe}_3$  and n-butyllithium in THF at  $-90^\circ\text{C}$ . The terminus at which new bond formation occurs in reactions of this ambident nucleophile appears to be determined by electronic and steric factors. Reactions of this reagent with trimethylchlorosilane, trimethyltin chloride, iodomethane, aqueous HCl, aldehydes (n- $\text{C}_6\text{H}_{13}\text{CHO}$ ,  $\text{PhCHO}$ ) and ketones ( $\text{CF}_3\text{C(O)CH}_3$ ,  $\text{PhC(O)CH}_3$ , cyclohexanone) were carried out.

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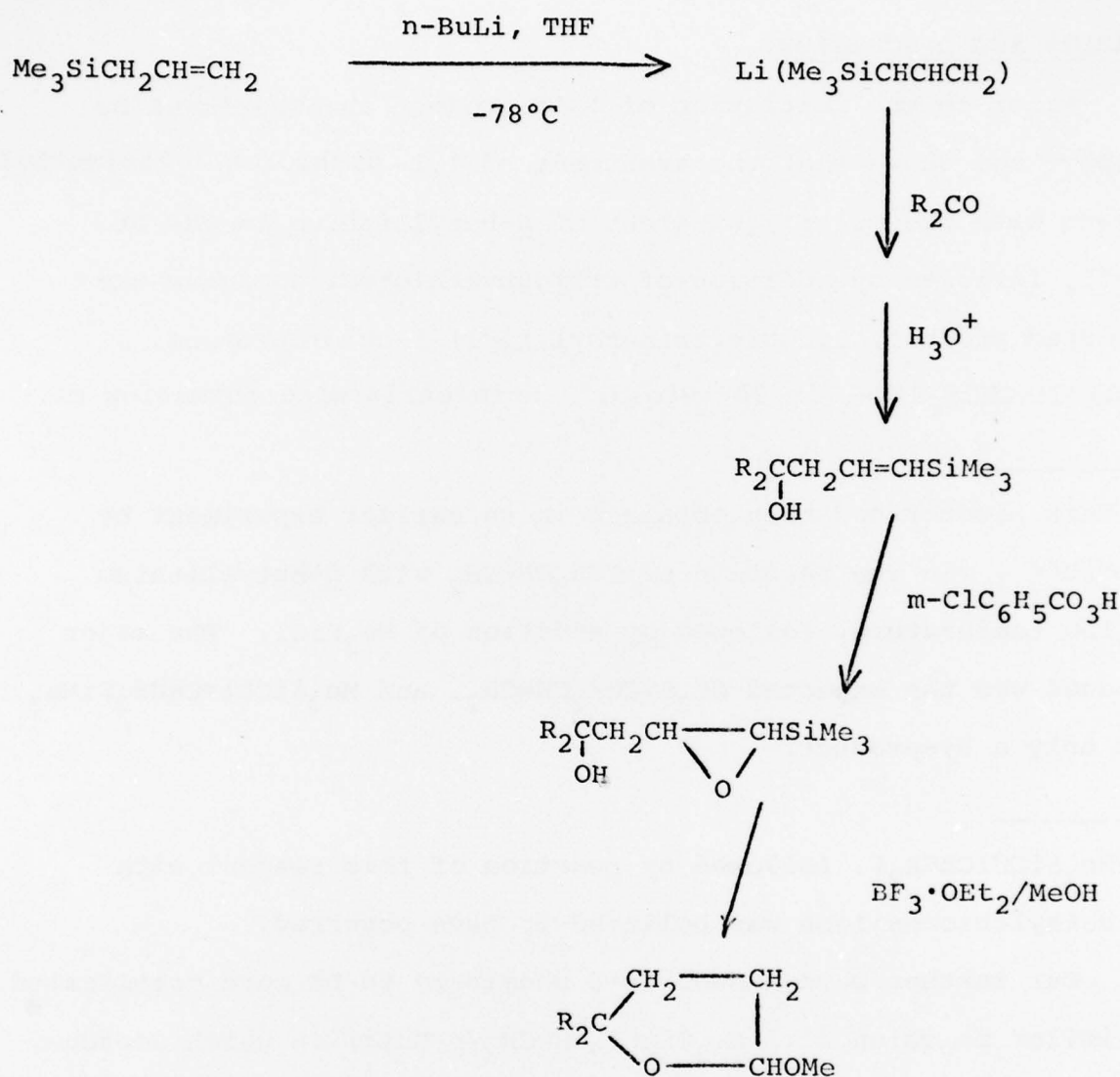
# National Science Foundation Graduate Fellow, 1973-1976.



## INTRODUCTION.

In a previous study we prepared the novel unsymmetrically substituted gem-dichloroallyllithium and studied its reactions with metal and metalloidal halides<sup>1</sup> and with aldehydes, ketones and other organic substrates<sup>2</sup>. Of particular interest was the regioselectivity of this ambident nucleophile, which in coupling or addition reactions could form the new bond to carbon either at the  $\text{CCl}_2$  or the  $\text{CH}_2$  terminus. During the course of this work we prepared 1,1-dichloroallyltrimethylsilane,  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ , which should be a precursor for another interesting unsymmetrically substituted allylic lithium reagent, gem-chloro(trimethylsilyl)allyllithium,  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ . The trimethylsilyl group is a substituent of some interest for three reasons. (1) It is a bulky group and the resulting steric factors could well lead to new bond formation at the  $\text{CH}_2$  terminus in all reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ . (2) The trimethylsilyl group is well known to stabilize an adjacent partial or full negative charge, presumably by delocalization of electron density into the vacant 3d orbitals of silicon<sup>3</sup>. Thus its electronic effect would tend in the direction of that of a chlorine substituent, and so one might expect to observe regioselectivity similar to that found for gem-dichloroallyllithium in those cases where steric factors are not predominant. (3) Finally, the lithium reagent obtained by lithiation of allyltrimethylsilane itself,  $\text{Li}(\text{Me}_3\text{SiCHCHCH}_2)$ ,<sup>4</sup> is a useful  $\beta$ -acylcarbanion equivalent, with the reaction sequence shown in Scheme 1 being used in its synthetic applications.<sup>5</sup> Noteworthy

Scheme 1



in this connection is that  $\text{Li}(\text{Me}_3\text{SiCHCHCH}_2)$  appears to react with aldehydes and ketones to form the new C-C bond exclusively at the  $\text{CH}_2$  terminus of the reagent. On steric grounds alone, one thus would expect all reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with carbonyl compounds to result in C-C bond formation at the  $\text{CH}_2$  end also.

We report here concerning the generation and some of the reactions of this interesting reagent.

## RESULTS AND DISCUSSION.

Prior to the initiation of this project an experiment by Murphy<sup>6</sup> had shown that the treatment of 1,1-dichloroallyltrimethylsilane with one molar equivalent of *n*-butyllithium in THF at -90°C, followed by addition of trimethylchlorosilane, gave the expected product, 1,3-bis(trimethylsilyl)-1-chloropropene,  $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{SiMe}_3$  in 90% yield.\* Straightforward formation of

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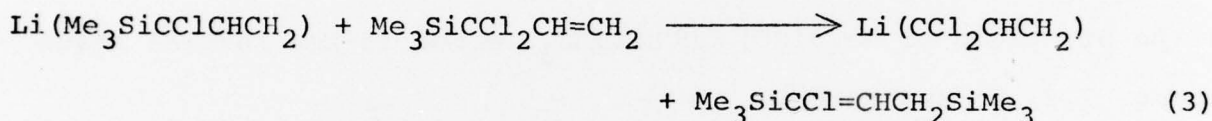
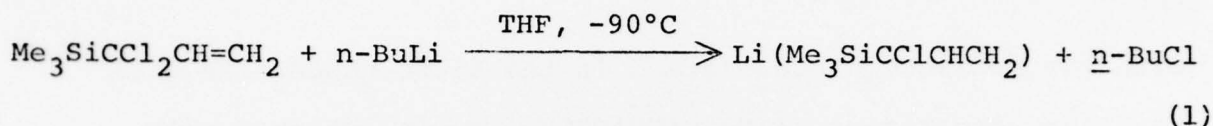
\* This product had been obtained in an earlier experiment by Woodruff<sup>7</sup>, via the reaction of  $\text{CCl}_3\text{CH}=\text{CH}_2$  with *n*-butyllithium at low temperature, followed by addition of  $\text{Me}_3\text{SiCl}$ . The major product was the expected  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ , and  $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{SiMe}_3$  was only a by-product.

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$\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ , followed by reaction of this reagent with trimethylchlorosilane was believed to have occurred.

Our further work showed this chemistry to be more complicated. A similar reaction (1:1  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2/\text{n-BuLi}$ ) in which acetone, rather than trimethylchlorosilane, was the substrate gave surprising results. The products of this reaction, after hydrolytic work-up were  $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{SiMe}_3$  (41%),  $\text{CH}_2=\text{CHCCl}_2\text{CMe}_2\text{OH}$  (46%) and  $\text{CH}_3(\text{CH}_2)_3\text{CMe}_2\text{OH}$ . None of the product expected from the addition of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  to acetone was obtained. One may rationalize these unexpected results in the following manner. *n*-Butyllithium does react with  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$  to form  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ . However, once formed, the latter then reacts with the starting material

at a rate equal to or greater than that of n-butyllithium to generate gem-dichloroallyllithium by a displacement reaction from silicon (eq. 1 and 2). Since each molar equivalent of n-butyllithium



consumes two of  $\text{Me}_3\text{SiCCl}_2\text{CH=CH}_2$  in this sequence, only one half of it will have been consumed when all of the starting silane has reacted. When acetone then is added to the reaction mixture, one half molar equivalent each of n-butyllithium and gem-dichloroallyllithium are present for it to react with. Thus all the observed products are explained, as is the absence of the expected alcohol product.

The results obtained when trimethylchlorosilane is used as substrate are "anomalous" and misleading because of the peculiarities of the relative rates of possible reactions in this system. When trimethylchlorosilane is added to such a reaction mixture derived from a 1:1  $\text{Me}_3\text{SiCCl}_2\text{CH=CH}_2/\text{n-BuLi}$  reaction, it apparently reacts rapidly with gem-dichloroallyllithium but only very slowly with n-butyllithium.\* However, n-butyllithium reacts rapidly

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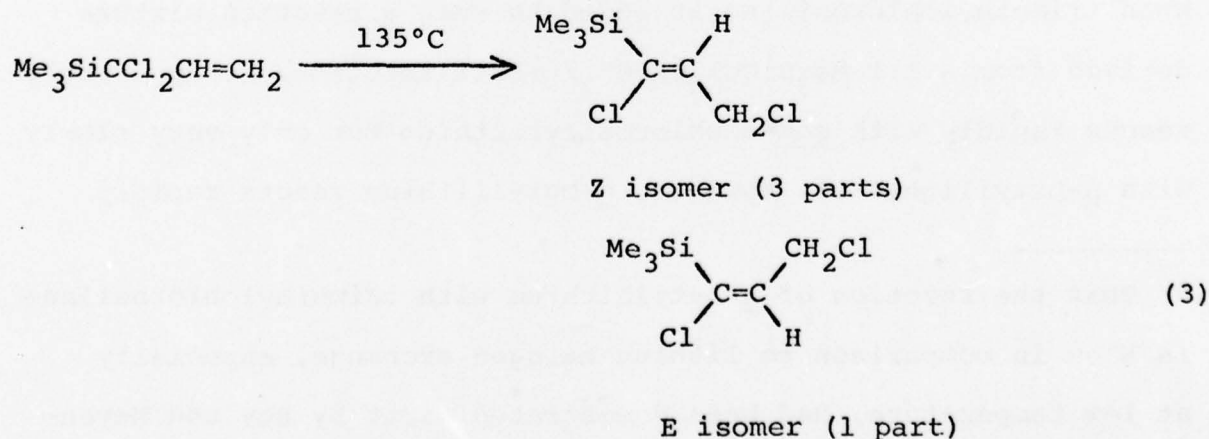
\* That the reaction of n-butyllithium with trimethylchlorosilane is slow in comparison to lithium-halogen exchange, especially at low temperature, had been demonstrated first by Bey and Weyenberg.<sup>8</sup>

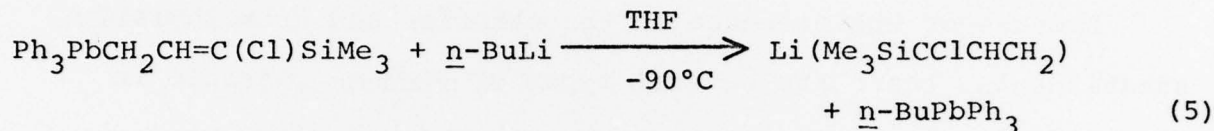
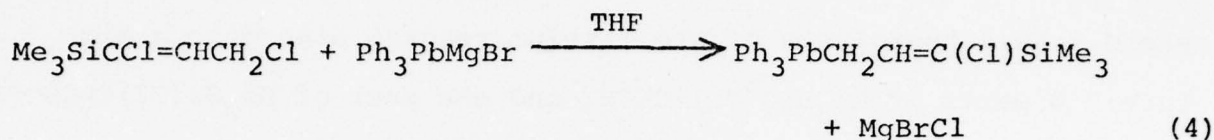
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with the  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$  formed in the  $\text{Li}(\text{CCl}_2\text{CHCH}_2)/\text{Me}_3\text{SiCl}$  reaction, generating  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  again, which reacts rapidly with the trimethylchlorosilane which is present. Thus the 50% yield of  $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{SiMe}_3$  formed in the initial stage (eq. 1,2) is augmented.

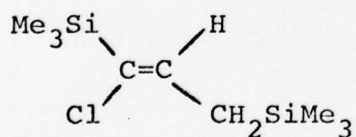
Clearly, because of these complications,  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$  is not a practical precursor for  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ . However, an alternate, less direct route to this reagent, based on the allylic rearrangement product of  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ , could be developed. We had prepared gem-dichloroallyllithium by the conversion sequence  $\text{CCl}_3\text{CH}=\text{CH}_2 \longrightarrow \text{CCl}_2=\text{CHCH}_2\text{Cl} \longrightarrow \text{CCl}_2=\text{CH}-\text{CH}_2\text{PbPh}_3 \longrightarrow \text{Li}(\text{CCl}_2\text{CHCH}_2)$ ,<sup>1,2</sup> and this strategy also was applicable in the synthesis of gem-chloro(trimethylsilyl)allyllithium (eq. 3-5). This procedure is not complicated by the oc-



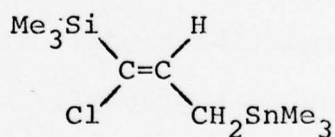


currence of side reactions, and the yields of products of the coupling and addition reactions of this reagent in general are high.

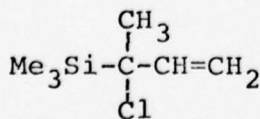
A study of the regioselectivity of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  was undertaken. In coupling reactions with trimethylchlorosilane and with trimethyltin chloride the only products which were isolated were those in which the Group IV element-to-carbon bond had been formed at the  $\text{CH}_2$  terminus of the reagent, I (98% yield) and II (85% yield), respectively. On the other hand, reaction with iodomethane gave a 4:1 mixture of III and IV in 81% total



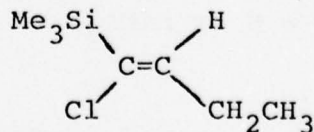
I



II



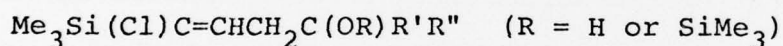
III



IV

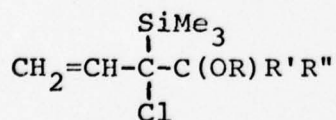
yield. Acid hydrolysis of the lithium reagent also gave a mixture: 3 parts of  $\text{Me}_3\text{SiC}(\text{Cl})=\text{CHCH}_3$  and one part of  $\text{Me}_3\text{Si}(\text{Cl})\text{CHCH}=\text{CH}_2$  in 78% total yield.

Because of the presence of the chlorine and trimethylsilyl substituents, there are several types of products possible in the reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with aldehydes and ketones. Reaction at the  $\text{CH}_2$  terminus should, after hydrolysis or treatment with trimethylchlorosilane, produce a stable product of type V. Reaction at the substituted end of the reagent is potentially more complicated. One possibility, of course, is

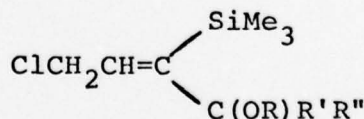


V

the straightforward addition product, VI. However, as an allylic chloride, VI has the potential to undergo allylic rearrangement to give VII. (This type of rearrangement occurred with some of the products of gem-dichloroallyllithium/ketone reactions, either under the reaction conditions or during isolation by distillation or gas chromatography).



VI (R = H or SiMe<sub>3</sub>)



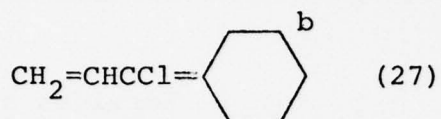
VII

A third possible type of product would be formed in a Peterson reaction<sup>9</sup> by elimination of trimethylsilanolate anion from



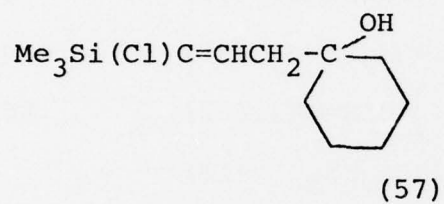
TABLE 1. Reactions of gem-Chloro(trimethylsilyl)allyllithium.

Substrate	Product (% Yield)	Terminus at which bond formation occurred	
		C(Cl)SiMe <sub>3</sub>	CH <sub>2</sub>
Me <sub>3</sub> SiCl	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> SiMe <sub>3</sub> (98)	0	100
Me <sub>3</sub> SnCl	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> SnMe <sub>3</sub> (85)	0	100
CH <sub>3</sub> I	Me <sub>3</sub> Si(Cl)(CH <sub>3</sub> )CCH=CH <sub>2</sub> (62)	80	20
	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> CH <sub>3</sub> (19)		
HCl	Me <sub>3</sub> Si(Cl)CHCH=CH <sub>2</sub> } Me <sub>3</sub> Si(Cl)C=CHCH <sub>3</sub> } (78)	26	74
CF <sub>3</sub> C(O)CH <sub>3</sub>	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> C(OH)(CF <sub>3</sub> )CH <sub>3</sub> (74)	--	74
PhCHO	CH <sub>2</sub> =CHCCl=CHPh <sup>b</sup> (26)	28	72
	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> CH(OH)Ph (67)		
PhC(O)CH <sub>3</sub> <sup>a</sup>	CH <sub>2</sub> =C(Ph)OSiMe <sub>3</sub> (10)		
	CH <sub>2</sub> =CHCCl=C(CH <sub>3</sub> )Ph <sup>b</sup> (43)		
	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> C(OH)(CH <sub>3</sub> )Ph (8)	67	33
	Ph <sub>2</sub> C(CH <sub>3</sub> )OSiMe <sub>3</sub> (19)		
	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> C(CH <sub>3</sub> )(Ph)OSiMe <sub>3</sub> (13)		
C <sub>6</sub> H <sub>13</sub> CHO	CH <sub>2</sub> =CHCCl=CHC <sub>6</sub> H <sub>13</sub> <sup>b</sup> (60)	68	32
	Me <sub>3</sub> Si(Cl)C=CHCH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>13</sub> (28)		



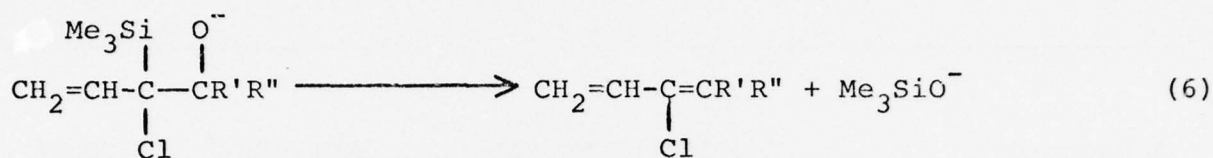
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68



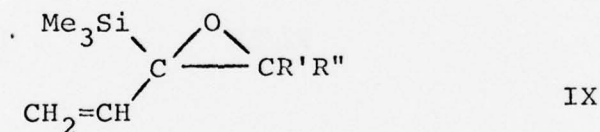
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- a. mixture treated with  $\text{Me}_3\text{SiCl}$  after addition of carbonyl.
- b. product of Peterson reaction, indicative of attack at the  $\text{C}(\text{Cl})\text{SiMe}_3$  terminus of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ . See text.

the initial adduct as shown in eq. 6. The intermediate adduct,



VIII

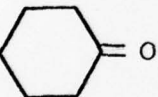
VIII, however, also could undergo another intramolecular reaction. Since chloride ion is a good leaving group, the carbon atom to which the chlorine is bound is susceptible to intramolecular  $\text{S}_{\text{N}}2$  attack by the alkoxide oxygen to give still another type of product, an oxirane, IX. The mechanism of this type of process



has been studied by Swain and coworkers.<sup>10</sup>

Reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with five selected carbonyl compounds were examined in order to have a basis for comparison with the carbonyl addition reactions of  $\text{Li}(\text{CCl}_2\text{CHCH}_2)$  on the one hand and with those of  $\text{Li}(\text{Me}_3\text{SiCHCHCH}_2)$  on the other. The products obtained in these reactions, as well as those of the coupling and protolysis reactions are given in Table 1. A comparison of available results for the three terminally substituted allylic lithium reagents is given in Table 2.

TABLE 2. Reactions of  $\text{Li}[\text{Me}_3\text{SiCClCHCH}_2]$ ,  $\text{Li}[\text{CCl}_2\text{CHCH}_2]$  and  $\text{Li}[\text{Me}_3\text{SiCHCHCH}_2]$  with Halide- and Carbonyl-containing Substrates.

Substrate	$\text{C}(\text{Cl})\text{SiMe}_3/\text{CH}_2$	$\text{CCl}_2/\text{CH}_2^2$	$\text{CHSiMe}_3/\text{CH}_2^{4,5}$
$\text{Me}_3\text{SiCl}$	0/100	100/0	0/100
$\text{Me}_3\text{SnCl}$	0/100	0/100	
$\text{CH}_3\text{I}$	80/20	100/0	0/100
$\text{HCl}$	26/74	100/0	35/65
$\text{CF}_3\text{C}(\text{O})\text{CH}_3$	a/74	0/100	
$\text{PhCHO}$	28/72	0/100	0/100 <sup>d</sup>
$\text{PhC}(\text{O})\text{CH}_3$	67/33	62/38	
$\text{RCHO}$	68/32 <sup>b</sup>	71/29 <sup>c</sup>	
	32/68	100/0	0/100

a. not determined. The 74% is an absolute yield

b.  $\text{R} = \text{C}_6\text{H}_{13}$

c.  $\text{R} = \text{C}_2\text{H}_5$

d. reaction with p-tolualdehyde

1,1,1-Trifluoroacetone reacted with gem-dichloroallyllithium to form the new C-C bond exclusively at the CH<sub>2</sub> terminus,<sup>2</sup> and, similarly, only the product resulting from reaction at the unsubstituted end of Li(Me<sub>3</sub>SiCClCHCH<sub>2</sub>) was observed. The reaction of Li(CCl<sub>2</sub>CHCH<sub>2</sub>) with benzaldehyde gave exclusively CCl<sub>2</sub>=CHCH<sub>2</sub>CH(Ph)OH<sup>2</sup>. Trimethylsilylallyllithium was similarly selective, giving, it was reported,<sup>5</sup> only the product from bond formation at the CH<sub>2</sub> terminus on reaction with p-tolualdehyde. On the other hand, Li(Me<sub>3</sub>SiCClCHCH<sub>2</sub>) was less selective, showing only a 72:28 preference for C-C bond formation at the CH<sub>2</sub> end. The results of the reactions of Li(Me<sub>3</sub>SiCClCHCH<sub>2</sub>) and Li(CCl<sub>2</sub>CHCH<sub>2</sub>) with acetophenone and n-alkyl aldehydes were very similar, both reagents showing a 2:1 preference for reaction at the substituted carbon. Finally, Li(Me<sub>3</sub>SiCClCHCH<sub>2</sub>) added to the C=O bond of cyclohexanone showing a ca. 2:1 preference for formation of the new C-C bond at the CH<sub>2</sub> terminus. gem-Dichloroallyllithium reacted with cyclohexanone exclusively at the CCl<sub>2</sub> end<sup>2</sup>, while the reaction of Li(Me<sub>3</sub>SiCHCHCH<sub>2</sub>) with this ketone was reported to give the alcohol derived from reaction at the CH<sub>2</sub> terminus as the sole product in 73% yield.<sup>5</sup>

Before examining the reasons for the difference in the regioselectivity of the three allylic lithium reagents under discussion, a brief review of the factors discussed for gem-dichloroallyllithium<sup>2</sup> is in order. It was established that the addition of Li(CCl<sub>2</sub>CHCH<sub>2</sub>) to carbonyl compounds is not a reversible process. Also to be noted in the work of Miginiac and coworkers<sup>11</sup>, who



found reversible carbonyl addition only with allylic lithium reagents such as  $\text{Li}(\text{CH}_2\text{CHCHR})$  ( $\text{R} = \text{Ph}, \text{CH}_2=\text{CH}$ ) in which extensive delocalization of negative charge was possible. Thus, one would expect that addition of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  to the  $\text{C}=\text{O}$  linkage also would be irreversible. In the case of gem-dichloroallyllithium it also was established with reasonable certainty that the carbonyl additions do not involve an electron transfer mechanism, and it was concluded that a polar, nucleophilic addition mechanism was operative.<sup>2</sup>

The regioselectivity of the addition of gem-dichloroallyllithium to carbonyl compounds showed a marked electronic effect. In experiments with substituted acetophenones it was found that electron-releasing substituents resulted in enhanced reaction at the  $\text{CCl}_2$  terminus of the reagent (vs. acetophenone), while electron-attracting substituents favored bond formation at the  $\text{CH}_2$  end. These results were rationalized in terms of Pearson's hard/soft acid/base approach (HSAB).<sup>12</sup> The  $\text{CCl}_2$  terminus of the gem-dichloro anion, with its electron-attracting chlorine substituents would be much more effective at delocalizing negative charge and, as such, is the "softer" end of the ambident lithium reagent. Thus, it should show a preference for reaction with "soft" electrophiles, such as dialkyl ketones with their two electron-releasing alkyl groups. Conversely, the  $\text{CH}_2$  end of the gem-dichloroallyl anion is the "harder" nucleophilic site and, as such, prefers to react with "hard" electrophilic centers such as carbonyl functions bearing inductively electron-withdrawing substituents such as

phenyl and trifluoromethyl. Thus reaction at the  $\text{CH}_2$  terminus of the reagent would be favored. The same approach was used recently by Miginiac and coworkers<sup>11d</sup> to rationalize the regioselectivity of  $\text{Li}(\text{MeEtCCHCH}_2)$  additions to aldehydes and ketones.

The reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with carbonyl compounds may also be examined in terms of the HSAB approach. The substituted end, with its chlorine and trimethylsilyl substituents, should have greater negative charge delocalization thus should be the "soft" terminus of the anion, while the  $\text{CH}_2$  end, as before, would be the "hard" nucleophilic site. Although the trimethylsilyl group is able to delocalize an adjacent negative charge (as mentioned in the Introduction), one would not necessarily expect it to be as efficient an electron-withdrawing group as the electronegative chlorine substituent. Therefore, one might expect that the difference between the "hard" and "soft" ends of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  would be somewhat less than the difference between the "hard" and "soft" ends of gem-dichloroallyllithium. Consequently, one would expect the reactions of the former reagent to be somewhat less regioselective than those of the latter. In addition,  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  is much more sterically hindered at its substituted end than is  $\text{Li}(\text{CCl}_2\text{CHCH}_2)$ . In view of the diminished electronic effect in  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ , it would not be surprising to see some assertion of the stronger steric effect in directing the course of reaction in this reagent.

The observed reactions of gem-chloro(trimethylsilyl)allyllithium (Table 1) lend support to these ideas. The results of



the coupling reactions with iodomethane and trimethylchlorosilane indicate the operation of strong steric effects. Both of these substrates reacted with gem-dichloroallyllithium to form products at the  $\text{CCl}_2$  terminus in reactions under kinetic control.<sup>1</sup> In the reaction of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with the unhindered iodomethane, formation of the new C-C bond at the substituted end of the reagent predominated by a factor of 4, but in its reaction with the hindered trimethylchlorosilane the only product obtained was the one formed at the  $\text{CH}_2$  terminus. In the case of the reactions with trimethyltin chloride we probably are dealing with products of thermodynamic control.<sup>1</sup>

1,1,1-Trifluoroacetone, with its highly electronegative  $\text{CF}_3$  group, possesses a relatively "hard" electrophilic center, and thus in its reaction with  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ , as in its reaction with  $\text{Li}(\text{CCl}_2\text{CHCH}_2)$ , the new C-C bond was formed, predominantly if not completely, at its  $\text{CH}_2$  end. The differences between  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  and  $\text{Li}(\text{CCl}_2\text{CHCH}_2)$  become more apparent in their reactions with less polarized electrophiles. The reactions of these reagents with acetophenone gave approximately the same product ratios for both reagents: 67/33 for  $\text{C}(\text{Cl})\text{SiMe}/\text{CH}_2$  vs. 62/39 for  $\text{CCl}_2/\text{CH}_2$ . The change in substrate to benzaldehyde involve a change from an electron-releasing methyl substituent on the carbonyl function to hydrogen. This change was enough to change the  $\text{CCl}_2/\text{CH}_2$  derived product ratio to 0/100 in the case of gem-dichloroallyllithium, but with  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  the  $\text{C}(\text{Cl})\text{SiMe}_3/\text{CH}_2$ -derived product ratio dropped only to 28/72. Alkyl aldehydes, apparently

similar electronically to acetophenone, gave similar results with both reagents:  $\text{CCl}_2/\text{CH}_2$  product ratio = 71/29 for propionaldehyde;  $\text{C}(\text{Cl})\text{SiMe}_3/\text{CH}_2$  ratio = 68/32 for *n*-heptaldehyde. With dialkyl ketones, including cyclohexanone, "softer" electrophiles, gem-dichloroallyllithium reacted to form the new C-C bond exclusively at the  $\text{CCl}_2$  end. Gem-chloro(trimethylsilyl)allyllithium was not as selective: its reaction with cyclohexanone gave a 32:68 mixture of products derived from reaction at the  $\text{C}(\text{Cl})\text{SiMe}_3$  and  $\text{CH}_2$  termini, respectively. Very likely steric effects are responsible for this result. In the phenyl-substituted carbonyl compounds the phenyl group is conjugated with, and thus coplanar with the carbonyl group. Thus, the carbonyl functions of benzaldehyde and acetophenone are free from steric hindrance above and below the plane of the molecule. However, the hindrance of the two alkyl groups attached to the carbonyl group of cyclohexanone, coupled with the steric hindrance due to the non-planar ring, appear to be sufficient to retard reaction at the bulky disubstituted carbon atom in  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$ .

It would also be of interest, as indicated in the introduction, to compare the results of this study with the data available for reactions of  $\text{Li}(\text{Me}_3\text{SiCHCHCH}_2)$  with aldehydes and ketones. However, in the reaction of this reagent with *p*-tolualdehyde, which was reported to give only  $\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}_3\text{-p})\text{OH}$ ,<sup>5</sup> the product yield was not specified. Its reaction with cyclohexanone gave X, which was claimed to be the sole product, in 74% yield.<sup>5</sup>

These results are somewhat surprising when compared with our reactions of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  with benzaldehyde and cyclohexanone. In the absence of full experimental details of these reactions of  $\text{Li}(\text{Me}_3\text{SiCHCHCH}_2)$ , a discussion of the regioselectivity of this reagent in the context of our results obtained with  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  would not be meaningful.

#### EXPERIMENTAL.

General Comments. All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. Rigorously dried solvents were used in all organolithium reactions. The reaction temperatures which are reported are uncorrected. They were obtained using a pentane (total immersion) thermometer immersed to a depth of about 3 cm in the stirred solution. The actual solution temperatures thus were about 8-10°C lower than the thermometer reading. Gas-liquid chromatography was employed for

collection of samples for analysis, spectroscopic measurements and refractive index determination and for yield determinations using internal standards and empirically determined response factors. Nuclear magnetic resonance spectra were recorded using a Varian Associates T60 or an Hitachi-Perkin Elmer R20-B high resolution spectrometer. Proton chemical shifts are reported in  $\delta$  units using tetramethylsilane (TMS) as internal standard. Infrared spectra were obtained using a Perkin Elmer 457A grating infrared spectrophotometer.

n-Butyllithium in hexane was purchased from Alfa/Ventron. The carbonyl compounds were commercial products (Aldrich or Eastman) and were used as received or purified if necessary. 1,1,1,3-Tetrachloropropane was purchased from PCR Chemicals, Inc. Trimethylchlorosilane was donated by Union Carbide Corp.

Characterizing data for new compounds prepared in this study are collected in Table 3.

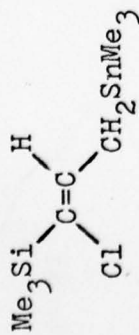
Preparation of 1,1-Dichloroallyltrimethylsilane.

The preparation of the title compound is a large scale adaptation of the small scale reaction first carried out by Murphy.<sup>1</sup> A 2 liter three-necked Morton flask, fitted with a pressure-equalizing dropping funnel, mechanical stirrer, and Claisen adapter, which allowed for both a low temperature thermometer and a nitrogen inlet, was charged with 132.9 g (243 mmol) of 3,3-dichloroallyltriphenyllead (prepared by the method of Murphy<sup>1,2</sup>), dissolved in 1.2 l of tetrahydrofuran (THF) (distilled from sodium benzophenone ketyl). The solution was cooled, with



TABLE 3. Characterization of New Compounds.<sup>a</sup>

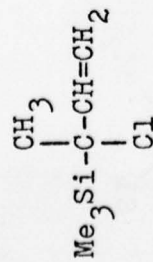
Compound	Mp (°C)	n <sub>D</sub> <sup>25</sup>	Analysis Carbon	found (calcd) Hydrogen	Proton NMR Spectrum (δ units, downfield from internal TMS). In CCl <sub>4</sub> .
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2\text{SiMe}_3^* \end{array}$		1.4529	49.18 <sup>b</sup> (48.93)	9.61 (9.58)	0.10 (s, 9H, Me <sub>3</sub> Si), 0.20 (s, 9H, Me <sub>3</sub> Si), 1.87 (d, J = 9Hz, 2H, CH <sub>2</sub> ), 6.01 (t, J = 9Hz, 1H, =CH)
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2\text{Cl} \end{array} \quad (\text{Z})$		1.4710	39.45 <sup>c,d</sup> (39.35)	6.61 (6.60)	0.23 (s, 9H, Me <sub>3</sub> Si), 4.22 (d, J = 7Hz, 2H, CH <sub>2</sub> ), 6.12 (t, J = 7Hz, 1H, =CH)
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{CH}_2\text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{H} \end{array} \quad (\text{E})$		1.4785			0.32 (s, 9H, Me <sub>3</sub> Si), 4.05 (d, J = 8Hz), 2H, CH <sub>2</sub> ), 6.55 (t, J = 8Hz, 1H, =CH)
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_2\text{PbPh}_3 \end{array}$	56-57°		49.17 <sup>e</sup> (49.17)	4.71 (4.64)	0.10 (s, 9H, Me <sub>3</sub> Si), 3.13 (d, J = 9Hz, 2H, CH <sub>2</sub> ), 6.45 (t, J = 9Hz, 1H, =CH), 7.45 (m, 15H, Ph <sub>3</sub> Pb)
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{CH}_3 \end{array}$		1.4432 <sup>f</sup>	48.73 <sup>f,g</sup> (48.46)	8.86 (8.81)	0.17 (s, 9H, Me <sub>3</sub> Si), 1.85 (d, J = 6Hz, 3H, CH <sub>3</sub> ), 6.05 (q, J = 6Hz, 1H, =CH)
Me <sub>3</sub> SiCHClCH=CH <sub>2</sub>		1.4432 <sup>f</sup>			0.13 (s, 9H, Me <sub>3</sub> Si), 3.73 (d, J = 7Hz, 1H, CHCl), 4.93-6.00 (m, 3H, CH=CH <sub>2</sub> )



1.4966

$^{34.47^h}$   
(34.70)

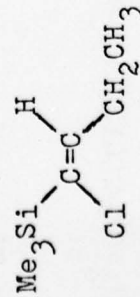
0.17 (s, 18H, Me<sub>3</sub>Si and Me<sub>2</sub>Sn, J(<sup>1</sup>H-<sup>119</sup>Sn) = 55Hz, J(<sup>1</sup>H-<sup>117</sup>Sn) = 51 Hz), 2.04 (d, J = 9Hz, 2H, CH<sub>2</sub>), 6.22 (t, J = 9Hz, 1H, =CH)



60-61°

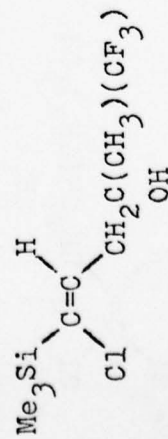
$^{51.70^i,j}$   
(51.66)

0.15 (s, 9H, Me<sub>3</sub>Si), 1.63 (s, 3H, CH<sub>3</sub>), 4.91-6.22 (m, 3H, CH=CH<sub>2</sub>)



1.4462

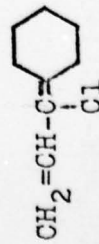
0.20 (s, 9H, Me<sub>3</sub>Si), 1.07 (t, J = 7Hz, 3H, CH<sub>3</sub> of Et), 2.34 (m, 2H, CH<sub>2</sub>), 5.95 (t, J = 7Hz, 1H, =CH)



1.4295

$^{41.58^k}$   
(41.46)

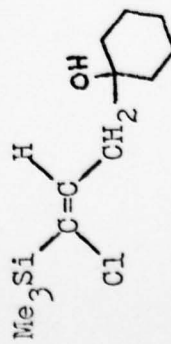
0.23 (s, 9H, Me<sub>3</sub>Si), 1.37 (s, 3H, CH<sub>3</sub>), 1.99 (s, 1H, OH), 2.58-2.82 (m, 2H, CH<sub>2</sub>), 6.11 (t, J = 7Hz, 1H, =CH)



1.5302

$^{68.89^l}$   
(69.00)

1.63 (s, 6H), 2.28-2.70 (m, 4H), 5.03-7.00 (m, 3H, CH=CH<sub>2</sub>)



1.4983

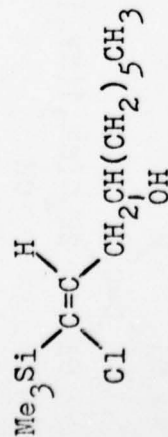
0.22 (s, 9H, Me<sub>3</sub>Si), 0.93-2.07 (m, 11H, cyclohexyl H and OH), 2.42 (d, J = 7Hz,

2H, CH<sub>2</sub>), 6.03 (t, J = 7Hz, 1H, =CH)



1.4759 69.57<sup>m</sup> 9.93  
(69.55) (9.92)

0.70-1.73 (m, 11H, C<sub>5</sub>H<sub>11</sub>), 2.05-2.83(m, 2H, allylic CH<sub>2</sub>), 5.03-6.90 (m, 4H, =CH)



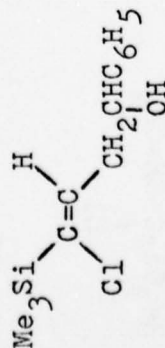
1.4698

0.23 (s, 9H, Me<sub>3</sub>Si), 0.65-1.58 (m, 14H, C<sub>6</sub>H<sub>13</sub>, OH), 2.28-2.58 (m, 2H, allylic CH<sub>2</sub>), 3.48-3.85 (m, 1H, HOCH<sub>2</sub>), 6.00 (t, J = 7Hz, 1H, =CH)



1.5985<sup>n</sup>

5.12-6.85 (m, 4H, =CH), 6.88 (s, 5H, C<sub>6</sub>H<sub>5</sub>)



1.5306

61.37 7.46  
(61.27) (7.52)

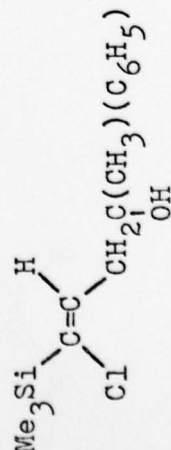
0.18 (s, 9H, Me<sub>3</sub>Si), 1.63 (s, 1H, OH), 2.65 (t, J = 7Hz, 2H, CH<sub>2</sub>), 4.78 (t, J = 7Hz, 1H, HOCH<sub>2</sub>), 6.03 (t, J = 7Hz, 1H, =CH), 7.25 (s, 5H, C<sub>6</sub>H<sub>5</sub>)



1.5818

74.04 6.35  
(73.95) (6.20)

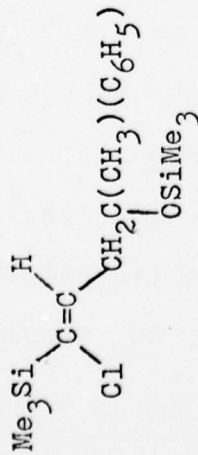
2.27 and 2.35 (2 s, 3H, CH<sub>3</sub> of E and Z isomers), 4.97-6.93 (m, 3H, CH<sub>2</sub>=CH), 7.27 (s, 5H, C<sub>6</sub>H<sub>5</sub>)



1.5196

0.08 (s, 9H, Me<sub>3</sub>Si), 1.40 (s, 1H, OH), 1.50 (s, 3H, CH<sub>3</sub>), 2.70 (d, J = 7Hz, 2H, CH<sub>2</sub>),





1.4976

5.85 (t, J = 7 Hz, 1H, =CH),  
7.15 (s, 5H, C<sub>6</sub>H<sub>5</sub>)

0.13 (s, 18H, Me<sub>3</sub>Si), 1.65 (s, 3H, CH<sub>3</sub>), 2.72 (d, J = 6Hz, CH<sub>2</sub>), 5.88 (t, J = 6Hz, =CH), 7.28 (s, 5H, C<sub>6</sub>H<sub>5</sub>)

<sup>a</sup> Infrared spectra are recorded in: R. E. Mammarella, Ph.D. Thesis, Massachusetts Institute of

Technology, 1977. <sup>b</sup>Cl found, 16.20; calcd., 16.05. <sup>c</sup> Analysis of Z/E isomer mixture. <sup>d</sup>Cl found,

38.67; calcd., 38.71. <sup>e</sup> %Cl found, 5.88; calcd., 6.05. <sup>f</sup> For a 74/26 Me<sub>3</sub>SiC(Cl)=CHCH<sub>3</sub>/Me<sub>3</sub>SiCHClCH=CH<sub>2</sub> isomer mixture. <sup>g</sup> %Cl found, 23.64; calcd., 23.84. <sup>h</sup> %Cl found, 11.46; calcd., 11.38. <sup>i</sup> For a 77/23 mixture of Me<sub>3</sub>Si(CH<sub>3</sub>)(Cl)CCH=CH<sub>2</sub> and Me<sub>3</sub>SiC(Cl)=CHCH<sub>2</sub>CH<sub>3</sub>. <sup>j</sup> %Cl found, 21.57; calcd., 21.79. <sup>k</sup> %Cl found, 13.50; calcd., 13.60. <sup>l</sup> %Cl found, 22.61; calcd., 22.63. <sup>m</sup> %Cl found, 20.00; calcd., 20.53. <sup>n</sup> lit.<sup>19</sup> <sup>n</sup><sub>lit.</sub> <sup>25</sup> 1.5993.

$n_{lit.}^{19} n^{25D} 1.5993.$

stirring, to  $-93^{\circ}$ , after which a solution of n-butyllithium in hexane (ca. 243 mmol, Ventron, determined as 2.21 M by Gilman titration) was added dropwise over a 20 minute period. The light amber solution was stirred at  $-93 \pm 2^{\circ}$  for 75 min. after the addition of the n-butyllithium was completed and then 38.1 ml (ca. 300 mmol) of trimethylchlorosilane was added dropwise at this temperature over a 15 min. period. The color of the reagent was discharged before the addition of the trimethylchlorosilane was complete. The reaction mixture was allowed to warm slowly to room temperature and hydrolyzed by the addition of saturated ammonium chloride solution to a dry endpoint. The light yellow organic layer was filtered, concentrated to about 300 ml by rotary evaporation, and trap-to-trap distilled ( $25^{\circ}$ , 0.03 mm Hg) with only gradual warming of the distillation pot at the end of the distillation, leaving a residue of 119.6 g (99.6%) of n-butyltriphenyllead. GLC examination (20% SE 30) of the distillate showed the presence of small amounts of phenyltrimethylsilane and the disubstituted product,  $\text{Me}_3\text{Si}(\text{Cl})-\text{C}=\text{CHCH}_2\text{SiMe}_3$ . The distillate was concentrated by rotary evaporation and transferred with pentane washings to a large sublimier. The residual solvent was removed at 10 mm Hg into a dry ice/acetone-cooled trap connected between the sublimier and the vacuum manifold. Sublimation ( $25^{\circ}$ , 0.06 mm Hg) yielded, in two crops, 31.5 g (71%) of 1,1-dichloroallyltrimethylsilane, mp  $63-64^{\circ}$ , lit.<sup>1</sup> mp  $64-65^{\circ}$ ; NMR spectrum matched that of an authentic sample. NMR ( $\text{CCl}_4$ ):  $\delta$  0.23 (s, 9H,  $\text{SiMe}_3$ ), 5.10-6.30 (m, 3H, vinyl)

ppm downfield from TMS.

Reaction of 1,1-Dichloroallyltrimethylsilane with n-Butyllithium.

(a) Trimethylchlorosilane Quench.<sup>6</sup>

A 500 ml, three-necked Morton flask, equipped with a pressure-equalizing dropping funnel, a mechanical stirrer and a Claisen adapter which was fitted with a low-temperature thermometer and a nitrogen inlet tube, was charged with a solution of 3.66 g (20 mmol) of  $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$  in 300 ml of THF. The solution was cooled, with stirring, to  $-90^\circ$  while 9.5 ml of a solution of n-butyllithium in hexane ( $\sim 22.8$  mmol, Ventron Corp., 20.9 wt. %, determined as 2.4 M by Gilman titration) was added dropwise over a 5 min. period. The reaction mixture was stirred at  $-90^\circ$  for 15 min. and then 3.2 ml ( $\sim 25$  mmol) of trimethylchlorosilane was added dropwise. The resulting mixture was stirred and allowed to warm slowly to room temperature, then was hydrolyzed with saturated aqueous ammonium chloride to the dry end-point. GLC analysis (20% SE 30 at  $146^\circ$ ) of the concentrated organic layer showed the presence of 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene,  $\text{Me}_3\text{SiCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ , in 90% yield. A sample for characterization was isolated by GLC,  $n_D^{25}$  1.4529 (Woodruff<sup>7</sup>,  $n_D^{25}$  1.4527).

(b) Acetone Quench with Dilute Hydrochloric Acid Workup.

In similar fashion, a solution of 1.39 g (7.65 mmol) of 1,1-dichloroallyltrimethylsilane dissolved in 200 ml of THF was cooled to  $-91^\circ$  and treated with a solution of n-butyllithium

in hexane (ca. 8.03 mmol, 5% excess), dropwise over a 10 min period. The resulting clear, peach-colored solution was stirred for an additional 30 min at  $-91^{\circ}$ . Then, 1.90 ml (ca. 25 mmol) of anhydrous acetone was added over a two min period and the solution became colorless. After stirring for 5 min at  $-91^{\circ}$ , 50 ml of 1N hydrochloric acid was added by syringe over a 2 min period to produce a white slush at  $-20^{\circ}$ . On warming for an additional 15 min, the mixture became a clear, homogeneous solution. The reaction mixture was extracted with 300 ml of diethyl ether and 200 ml of water. The organic layer was washed with two 500 ml portions of water, dried over  $\text{MgSO}_4$ , and filtered. The filtrate was concentrated by rotary evaporation at reduced pressure. GLC analysis of the concentrate (20% SE30 on Chromosorb P at  $110^{\circ}$ ) showed the presence of three major products: a significant amount of 2-methyl-2-hexanol,  $\text{CH}_3(\text{CH}_2)_3\text{CMe}_2\text{OH}$ , (NMR spectrum and GLC retention time match those of an authentic sample, NMR spectrum matches published spectrum<sup>13</sup>); 3.52 mmol (46%) of 1,1-dimethyl-2,2-dichloro-3-buten-1-ol,  $\text{CH}_2=\text{CHCCl}_2\text{CMe}_2\text{OH}$ ,  $n_D^{25}$  1.4810, lit.<sup>2</sup>  $n_D^{25}$  1.4818, also NMR spectrum,<sup>2</sup> and 3.14 mmol (41%) of 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{SiMe}_3$ ,  $n_D^{25}$  1.4528, lit.<sup>7</sup>  $n_D^{25}$  1.4527.

Thermal Isomerization of 1,1-Dichloroallyltrimethylsilane.

The Preparation of 1,3-Dichloro-1-trimethylsilylpropene.

A flame-dried and nitrogen-flushed bomb tube (1/2 inch o.d. thick-walled glass tubing) was charged with 1.60 g (8.75 mmol) of 1,1-dichloroallyltrimethylsilane and sealed in vacuo. After it



had been heated in a bomb furnace at  $135 \pm 2^\circ$  for 20 hours, the tube was removed, cooled to room temperature and opened. GLC analysis (20% SE 30 at  $110^\circ$ ) of the amber liquid showed the presence of only two compounds, whose proton NMR spectrum showed them to be the E and Z forms of 1,3-dichloro-1-trimethylsilylpropene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{Cl}$ . The NMR spectrum matched that first observed by Murphy,<sup>6</sup> showing the same E/Z ratio of 1:3. A total of 1.50 g (94%) of the mixed isomers was recovered from the bomb tube.

On a preparative scale, since the routine purification of 3,3-dichloroallyltrimethylsilane is tedious, wasteful of material, and synthetically pointless, the isomerization step was generally carried out on material contaminated with 5-15% of impurities consisting of phenyltrimethylsilane and 2,2,6,6-tetramethyl-3-chloro-2,6-disila-3-heptene. These impurities necessitated more vigorous reaction conditions to effect complete isomerization (e.g., 43 hours at  $165^\circ$ ). The resulting solution generally was dark amber in color. Trap-to-trap distillation ( $25^\circ$ , 0.03 mm Hg, pot heated to ca.  $50^\circ$  at end of distillation) afforded a clear, colorless liquid which could be analyzed by GLC to determine the amount of 1,3-dichloro-1-trimethylsilylpropene available for succeeding reactions. For example, GLC analysis (20% SE30 at  $110^\circ$ ) of such a reaction mixture showed that it contained 5% of phenyltrimethylsilane and 3% of 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene.

Z and E Isomer Assignments

The NMR spectrum of the  $\text{Me}_3\text{Si}(\text{Cl})=\text{CHCH}_2\text{Cl}$  isomers showed the vinyl proton resonance at  $\delta 6.12$  (t,  $J = 7\text{Hz}$ ), the other at

$\delta$ 6.55 ppm (t,  $J = 8$  Hz).

The isomer assignments were made on the basis of the NMR field positions of the vinyl protons of the two species. The actual values were compared to the values calculated according to the equation  $\delta_{\text{C=CH}} = 5.25 + \sum Z$ , where the Z-factors are the substituent shielding coefficients.<sup>14</sup> The Z-factors for the chlorine and chloromethyl substituents were reported by Matter and co-workers<sup>14</sup> and the Z-value for the trimethylsilyl group was later determined by Chan and co-workers.<sup>15</sup> The field position of the vinyl proton was calculated to be 6.19 for the Z isomer and 6.46 for the E isomer. Comparison with the observed values (6.12 and 6.55) clearly shows that the major isomer is the Z isomer and the minor isomer is the E isomer.

The method can be extended as well to the  $\text{CH}_2$ -ended addition products of the transmetalation reactions. All of the products show only one silicon-methyl resonance in the NMR spectra and, as closely as can be seen, only one vinyl resonance, indicating the presence of only one isomer. Using the trimethylsilyl and chloromethyl Z-factors as before, but substituting the alkyl for the chloromethyl Z-factor, one obtains a field position of 5.94 ppm for the Z-isomers and 6.23 ppm for the E isomers. Out of the nine  $\text{CH}_2$ -ended addition products, seven show a vinyl resonance in the range of 5.88-6.05 ppm, clearly indicative of the Z isomers.

The two exceptions are the products derived from the reactions with 1,1,1-trifluoroacetone and trimethyltin chloride. The vinyl resonance of the 1,1,1-trifluoroacetone addition product is at 6.11 ppm. However, one might expect that the deshielding

effect of the highly electronegative trifluoromethyl group might move the vinyl resonance downfield somewhat, so that value is probably in the same range as the others. The trimethyltin chloride-derived addition product shows a vinyl resonance of 6.22 ppm. A close examination of the list of Z-factors, though, shows that they vary widely. The  $\text{CH}_2\text{Sn}$  substituent on the double bond is probably sufficiently different from a simple alkyl substituent that the calculation is not applicable to the tin compound. No  $\text{CH}_2\text{Sn}$  Z-factor is available, so the method cannot be used for that compound. It seems reasonable to assume that its configuration is the same as all of the others and, therefore, this product is the Z isomer.

For the case of the lead compound,  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ , the above method is also inapplicable. Again only one isomer is apparent in the NMR spectrum of the final pure product. However, in the NMR spectrum of the crude oil before crystallization, there is a second small doublet, 0.50 ppm upfield from the methylene doublet and an additional silicon-methyl resonance 0.08 ppm downfield from the principal silicon-methyl peak. The additional peaks are related to the principal resonances just as the resonances of the E isomer of  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{Cl}$  are related to those of the Z isomer, and therefore, probably represent the E isomer of the allyllead compound (comprising about 15% of the crude oil). Only the Z isomer is obtained on crystallization. Additionally, one must consider that the preparation of the lead compound involves the reaction of triphenylleadmagnesium bromide with predominantly Z- $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{Cl}$ . Since the reaction does



not involve the double bond, there is no reason to expect a change of configuration during the reaction. Using these observations, it is reasonable to assign the crystalline lead compound as the Z isomer.

The Reaction of Triphenylleadmagnesium Bromide with 1,3-Dichloro-1-trimethylsilylpropene. Preparation of 3-Chloro-3-trimethylsilylallyllead.

A one-liter, three-necked Morton flask, fitted with a 250 ml pressure-equalizing dropping funnel, mechanical stirrer, and reflux condenser topped with a nitrogen inlet, was charged with 13.05 g (537 mmol) of magnesium turnings and 600 ml of THF. The dropping funnel was charged with 88.5 g (564 mmol) of bromobenzene which was added dropwise (after initiation) at such a rate as to maintain a gentle reflux. The resulting Grignard solution was stirred under nitrogen overnight. The reaction vessel containing the magnesium metal-free phenylmagnesium bromide was cooled with an ice-water bath and 44.7 g (161 mmol) of lead dichloride (Baker, reagent, ground to a fine powder) was added at once as rapidly as possible. The reaction mixture was stirred vigorously for 30 min at ice bath temperature, and then for 3.5 hr at room temperature to dissolve all of the lead dichloride. The triphenylleadmagnesium bromide solution thus prepared then was cooled with an ice bath. Freshly prepared 1,3-dichloro-1-trimethylsilylpropene [33.8 g (185 mmol)] was added all at once to the cooled Grignard solution. Almost

immediately, the pea green color of the lead-Grignard reagent faded and was replaced by a light gray. The reaction mixture was stirred at ice bath temperature for 1 hour, allowed to warm to room temperature overnight, and then was hydrolyzed with ca. 85 ml of saturated ammonium chloride solution to a dry endpoint. Filtration and washing of the magnesium salts with two 100 ml portions of THF yielded a light yellow organic layer which was concentrated under reduced pressure. The residue was extracted with 500 ml of chloroform. The extracts were dried over magnesium sulfate, filtered, and concentrated by rotary evaporation to give a yellow oil. The oil was pumped on for 48 hr at 0.03 mm Hg to remove any traces of volatiles. The insertion of a syringe needle into the clear yellow oil initiated the crystallization of the product. After a thick slurry had formed, 25 ml of cold pentane was added and the mixture was filtered. Four crops of crystals were obtained in this manner to yield a total of 71.10 g (75%) of 3-chloro-3-trimethylsilylallyltriphenyllead,  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})-\text{SiMe}_3$ , mp 56-57°.

The Reaction of 3-Chloro-3-trimethylsilylallyltriphenyllead with n-Butyllithium: Trimethylchlorosilane Quench.

A 500 ml, three-necked, Morton flask, fitted with a mechanical stirrer, no air-stopper, and a Claisen adapter which allowed for a low temperature thermometer and a nitrogen inlet was charged with 7.675 g (13.1 mmol) of 3-chloro-3-trimethylsilylallyltriphenyllead dissolved in 200 ml of THF. The solution was cooled to -92°,

after which a solution of 2.26M n-butyllithium in hexane (ca. 13.5 mmol) was added dropwise over a 5 minute period. During the initial stages of the addition the solution was a clear, bright orange color which gradually shifted to a medium amber color after 30 minutes stirring at  $-92^{\circ}$ . Then 18 mmol of trimethylchlorosilane was added rapidly to the reaction mixture. Over a 5 min. period following the addition the solution color shifted from amber, through light olive, then gray, and finally to light blue. The light blue color remained during 15 minutes of stirring at  $-90^{\circ}$ , although the intensity diminished somewhat. After 30 minutes at  $-90^{\circ}$ , the blue color had almost completely vanished. The reaction mixture then was allowed to warm slowly to room temperature. The resulting clear, colorless solution was hydrolyzed to a dry end-point with 1.6 ml of saturated ammonium chloride solution, filtered, and trap-to-trap distilled at 0.05 mm Hg,

leaving a residue of 6.45 g (99%) of n-butyltriphenyllead. GLC analysis (4' UCW 98,  $100^{\circ}$ , tridecane internal standard) of the distillate showed the presence of 12.8 mmol (98%) of Z-2,2,6,6-tetramethyl-3-chloro-2,6-disila-3-heptene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{SiMe}_3$  whose IR and NMR spectra matched those of an authentic sample.

Hydrolysis of gem-Chloro(trimethylsilyl)allyllithium.

The lithium reagent was prepared as described above from 6.95 g (11.8 mmol) of  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$  at  $-92^{\circ}$ . The reagent solution was treated at this temperature with a solution containing 3.0 ml (36 mmol) of concentrated hydrochloric acid, 2.0 ml of water (as a

diluent), and 10 ml of THF. The resulting solution was stirred for 25 min at  $-90^{\circ}$ , during which time the color faded to pale yellow. The reaction mixture then was allowed to warm slowly to room temperature, to give a clear, colorless solution. This solution was extracted with 200 ml of pentane and 300 ml of water. The organic layer was washed with two 500 ml portions of water, and dried over magnesium sulfate. This mixture was filtered and trap-to-trap distilled (0.05 mm Hg, room temperature), leaving 5.55 g (95%) of n-butyltriphenyllead. GLC analysis of the distillate (4' UCW-98 at  $60^{\circ}$ , n-decane as the internal standard) showed the presence of 9.20 mmol (78%) of the combined isomers. NMR analysis ( $\text{CCl}_4$  as solvent) showed a Z-1-chloro-1-trimethylsilylpropene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_3$ , to 3-chloro-3-trimethylsilylpropene,  $\text{Me}_3\text{Si}(\text{Cl})\text{CHCH}=\text{CH}_2$ , ratio of 74/26.

Other Reactions of gem-Chloro(trimethylsilyl)allyllithium.

(a) With Trimethyltin Chloride.

The lithium reagent solution was prepared as described above from 7.30 g (12.4 mmol) of  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ . To this solution, at  $-92^{\circ}$ , was added 3.40 g (17 mmol) of solid trimethyltin chloride. After 5 minutes of vigorous stirring, the trimethyltin chloride crystals had completely dissolved and the solution color had faded to a light yellow. The reaction mixture was stirred for an additional 5 minutes at  $-90^{\circ}$  and then was allowed to warm slowly to room temperature. The light yellow, slightly cloudy mixture was transferred by cannula to a tared 500 ml, single necked, flame-dried and nitrogen-flushed flask which



then was fitted to a flame-dried and nitrogen-flushed trap-to-trap apparatus. The reaction mixture was trap-to-trap distilled ( $25^{\circ} - 100^{\circ}\text{C}$  at  $0.02\text{ mm Hg}$ ),

leaving a residue of 6.60 g which corresponds to a 99% yield of *n*-butyltriphenyllead and lithium chloride. GLC analysis of the distillate (20% SE 30 at  $120^{\circ}$ ; tetradecane internal standard) showed the presence of a small amount of phenyltrimethyltin and 10.54 mmol (85%) of *Z*-2,2,6,6-tetramethyl-3-chloro-2-sila-6-stanna-3-heptene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{SnMe}_3$ .

(b) With Iodomethane.

To a THF solution of the lithium reagent prepared as described above from 5.23 g (8.9 mmol) of  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ , at  $-90^{\circ}$ , was added 1.0 ml (ca. 15 mmol) of iodomethane over a 2 min period. The resulting brown solution was stirred at  $-90^{\circ}$  for 15 min, then allowed to slowly warm to room temperature. The clear, bright yellow mixture was trap-to-trap distilled ( $0.04\text{ mm Hg}$ ),

leaving a pot residue of 5.0 g, which corresponds to a 98% yield of *n*-butyltriphenyllead and lithium iodide. GLC analysis of the distillate (6' UCW-98 at  $58^{\circ}$ , *n*-decane internal standard) showed the presence of 5.52 mmol (62%) of 2-chloro-2-trimethylsilyl-3-butene,  $\text{Me}_3\text{Si}(\text{Cl})(\text{CH}_3)\text{CCH}=\text{CH}_2$ , and some *Z*-1-chloro-1-trimethylsilyl-1-butene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{CH}_3$ . NMR analysis ( $\text{CCl}_4$ ) was used to determine a 77/23 ratio for the  $-\text{C}(\text{Cl})\text{Si}(\text{CH}_3)_3/-\text{CH}_2$



ended addition products. This corresponds to a total yield of 81%. Samples of the pure isomers were collected by GLC.

(c) With Carbonyl Compounds.

i) Hydrolytic Work-up. The reaction with 1,1,1-trifluoroacetone is described to illustrate the procedure used.

To the lithium reagent, prepared as described above from 7.402 g (12.6 mmol) of  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ , was added at  $-90^\circ$ , by syringe over a two-min. period, 1.35 ml (15 mmol) of 1,1,1-trifluoroacetone (Aldrich). After all of the ketone was added, the solution color became clear and colorless. The reaction mixture was stirred at  $-90^\circ$  for 5 minutes and then hydrolyzed by the rapid addition of 50 ml of 1N HCl. The resulting mixture was allowed to warm to room temperature and extracted with 300 ml of diethyl ether and 200 ml of water. The organic layer was washed with two 500 ml portions of water, and then concentrated by rotary evaporation to ca. 50 ml. At this point, 250 ml of carbon tetrachloride was added. The mixture was dried over magnesium sulfate, filtered, and trap-to-trap distilled ( $25^\circ$ , 0.07 mm Hg ),

leaving a residue of 5.10 g (82%) of n-butyltriphenyllead. GLC analysis of the distillate (20% SE 30 at  $120^\circ$ ; dodecane internal standard) showed the presence of 9.32 mmol (74%) of Z-1-chloro-1-trimethylsilyl-4-methyl-4-trifluoromethylbuten-4-ol,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{C}(\text{OH})(\text{CF}_3)\text{CH}_3$ , the only high boiling product of the reaction.

The 74% yield for that reaction suggests that some of the allyl anion may have been diverted into side reactions. Small

amounts of enolization may have occurred, as was seen in the reactions with acetophenone, or there may have been some addition at the substituted end of the anion, resulting in a product which presumably would undergo a Peterson reaction to form  $\text{CH}_2=\text{CHCCl}=\text{C}(\text{Me})\text{CF}_3$ . That compound would probably be low boiling enough to lie under the solvent peak and thus it might not be detectable by GLC analysis or by NMR analysis of a reaction concentrate. In any case, the 74% yield does indicate a predominant, if not complete, preference for reaction at the  $\text{CH}_2$  end of  $\text{Li}(\text{Me}_3\text{SiCClCHCH}_2)$  by 1,1,1-trifluoroacetone.

A similar procedure was used in reactions of this lithium reagent with cyclohexanone, *n*-heptaldehyde and benzaldehyde.

ii) Trimethylchlorosilane Work-up. To the lithium reagent, which had been prepared at  $-90^\circ$  from 8.00 (13.7 mmol) of  $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$  in 200 ml of THF was added, dropwise, 1.91 ml (16.4 mmol) of acetophenone. The solution color faded immediately. The mixture was stirred for 5 min at  $-90^\circ$  and then treated with 3.07 ml (63 mmol) of trimethylchlorosilane. The reaction mixture was stirred at  $-90^\circ$  for 15 min and then allowed to warm slowly to room temperature. After warming, the solution was heated and stirred at reflux for 2 hr to ensure the formation of the silyl ether. The solution then was cannulated into a dry, nitrogen-filled, 500 ml, round-bottomed flask and trap-to-trap distilled (0.05 mm Hg).

An aliquot was removed by cannula for GLC analysis and the remainder was concentrated by distillation at atmospheric

pressure to remove most of the volatiles. GLC analysis of the aliquot (4' SE 30, 180°, hexadecane internal standard) showed the presence of 1.40 mmol (10%) of  $\alpha$ -trimethylsiloxystyrene,  $\text{CH}_2=\text{C}(\text{Ph})\text{OSiMe}_3$ ,  $n_D^{25}$  1.5004, lit.  $n_D^{25}$  1.5001 (NMR spectrum matches published spectrum<sup>17</sup>); 5.90 mmol (43%) of 1-methyl-1-phenyl-2-chloro-1,3-butadiene,  $\text{CH}_2=\text{CHCCl}=\text{C}(\text{Me})\text{Ph}$ ,  $n_D^{25}$  1.5818; 1.10 mmol (8%) of Z-1-chloro-1-trimethylsilyl-4-phenyl-1-penten-4-ol,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{Ph}$ ,  $n_D^{25}$  1.5196; 2.54 mmol (19%) of 1,1-diphenyl-1-trimethylsiloxoethane,  $\text{Ph}_2\text{C}(\text{Me})\text{OSiMe}_3$ ,  $n_D^{20}$  1.5315, lit.  $n_D^{20}$  1.5310; and 1.82 mmol (13%) of Z-1-chloro-1-trimethylsilyl-4-phenyl-4-trimethylsiloxy-1-pentene,  $\text{Me}_3\text{Si}(\text{Cl})\text{C}=\text{CHCH}_2\text{C}(\text{Me})(\text{Ph})\text{OSiMe}_3$ ,  $n_D^{25}$  1.4976. The total yield was 93% and the substituted/unsubstituted ratio was 67/33. Samples for identification and characterization were collected by GLC.

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REFERENCES

1. D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Organometal. Chem.,
2. D. Seyferth, G. J. Murphy and B. Mauzé, J. Am. Chem. Soc., 99 (1977) 5317.
3. D. J. Peterson, Organometal. Chem. Rev. A, 7 (1972) 295.
4. (a) R. J. P. Corriu, J. Masse and D. Samate, J. Organometal. Chem., 93 (1975) 71.  
(b) R. J. P. Corriu, G. F. Lanneau, D. Leclercq and D. Samate, J. Organometal. Chem., 144 (1978) 155.
5. D. Ayalon-Chass, E. Ehlinger and P. Magnus, J. Chem. Soc., Chem. Commun. (1977) 772.
6. G. J. Murphy, Ph.D. Thesis, Massachusetts Institute of Technology, 1974.
7. R. A. Woodruff, Ph.D. Thesis, Massachusetts Institute of Technology, 1973.
8. A. E. Bey and D. R. Weyenberg, J. Org. Chem., 31 (1966) 2036.
9. D. J. Peterson, J. Org. Chem., 33 (1968) 780.
10. C. G. Swain, A. D. Ketley and R. F. W. Bader, J. Am. Chem. Soc., 81 (1959) 2353.
11. (a) F. Gerard and P. Miginiac, Bull. Soc. Chim. Fr. (1974) 1924.  
(b) F. Gerard and P. Miginiac, Bull. Soc. Chim. Fr. (1974) 2527;  
(c) F. Barbot and P. Miginiac, Tetrahedron Lett., (1975) 3829.

- (d) F. Barbot, C. H. Chan, and P. Miginiac, *Tetrahedron Lett.*, (1976) 2309.
12. R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, 89 (1967) 1827.
13. *Sadtler Standard Spectra*, 1973-1975 Supplement, Sadtler Research Laboratories, Inc., 1975, NMR #21,168.
14. U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Tetrahedron*, 25, (1969) 691.
15. T. H. Chan, W. Mychajloskij, and R. Amouroux, *Tetrahedron Lett.*, (1977) 1605.
16. C. R. Krüger and E. G. Rochow, *Angew. Chem.*, 75 (1963) 793.
17. C. R. Krüger and E. G. Rochow, *J. Organometal. Chem.*, 1, (1964) 470.
18. A. Wright and R. West, *J. Amer. Chem. Soc.*, 96 (1974), 3214.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) gem-Chloro(trimethylsilyl)allyllithium, $\text{Li}[\text{Me}_3\text{SiCClCHCH}_2]$ , was prepared by the transmetalation reaction between $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{C}(\text{Cl})\text{SiMe}_3$ and n-butyllithium in THF at $-90^\circ\text{C}$ . The terminus at which new bond formation occurs in reactions of this ambident nucleophile appears to be determined by electronic and steric factors. Reactions of this reagent with trimethylchlorosilane, trimethyltin chloride, iodomethane, aqueous HCl, aldehydes ( $n\text{-C}_6\text{H}_{13}\text{CHO}$ , $\text{PhCHO}$ ) and ketones ( $\text{CF}_3\text{C}(\text{O})\text{CH}_3$ , $\text{PhC}(\text{O})\text{CH}_3$ , cyclohexanone) were carried out.		

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